PLASMAS AND GASES

LOCALIZATION OF POLYMER CHAINS AT TWO PENETRABLE INTERFACES IN A CONSTANT MAGNETIC FIELD

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We investigate the polymer chain localization in the system of two penetrable interfaces in an external constant magnetic field within the mean-field approximation. The saturation of a polymer chain in the limiting case of zero bulk concentration is studied. We obtain a non-monotonous behavior of the amount of adsorbed polymers as a function of the distance between the interfaces.

The localization of polymer chains at surfaces or at penetrable interfaces is of great interest from both theoretical and technological standpoints because of its various applications. Penetrable interfaces reside in structured surfaces or in layered environments which can be formed in microphase separated block-copolymers and liquid crystalline or lipid systems. Here, the interfaces between two media can act as attractive and penetrable interfaces for both alternating and random copolymers, as has been shown previously [1]. The understanding of polymers in environments of multiple interfaces and/or constant magnetic field can lead to novel applications for the selection and the recognition of polymer properties [2–6].

In the adsorbed state, the conformations of localized chains are a result of the interplay between the adsorption energy, entropy reduction due to the confinement in the adsorbed state, and the excluded volume repulsion between the monomers [7]. The latter is responsible for the formation of large loops and tails and thus for an extended adsorption layer [8]. Only excluded volume of monomers leads to saturation effects at surfaces or interfaces. Thus, taking the excluded volume effects into account is most important to understand the physics of real polymers close to surfaces or interfaces.

Unfortunately, it is virtually impossible to solve the many-chain problem for the polymer adsorption including all effects of conformation statistics and excluded volume. On the other hand, the effects of excluded volume interactions can be understood using mean-field concepts (see, e.g., [7]), thus neglecting the fluctuation effects around the most probable polymer state function (ground state dominance) within a given geometry and external potentials. Generally, the mean field model can be considered as a versatile tool to understand the essential effects of excluded volume interactions in many-chain systems under geometric constraints, boundary conditions, and external potentials [7,9]. One of the merits of the mean-field model is to provide exact solutions of the corresponding stationary nonlinear Schrödinger equation (SNLSE) for piecewise constant potentials.

In this work, we will demonstrate a formalism for the exact solution of the mean-field polymer adsorption problem for the system of two penetrable potential traps in a constant magnetic field. We investigate the saturation behavior of polymers in such environments. At first, we introduce the model for the case of a (I) *single penetrable interface*, and then we present the exact solution for the case of (II) *two penetrable interfaces*.

It is well known that the polymer chain statistics is dominated by the ground state solution of the Edwards equation (see [10])

$$\lambda u(x) = -\frac{a^2}{6}\frac{d^2 u(x)}{dx^2} + \frac{1}{k_{\mathrm{B}}T}U_{\mathrm{ext}}(x)u(x) ,\tag{1}$$

where $u(x)$ is the part of the state function of a polymer chain associated with the eigenvalue λ, a is the length of a statistical (Kuhn) segment, $U_{\mathrm{ext}}(x)$ denotes the potential energy of a segment at the position x, and $k_{\mathrm{B}}T$ denotes the usual product of Boltzmann's constant and the absolute temperature. For simplicity, we have used only one spatial coordinate related to the symmetry of the potential. We will study plane interfaces, where the localization takes place in the direction perpendicular to the interfaces only. The ground-state dominance argument can be easily seen from the formal solution of the partition function for a chain given by

$$Z(x, x') = \sum_k \exp\{-N\lambda_k\}u_k(x)u_k(x'),\tag{2}$$

where the index k counts the various solutions of Eq. (1). Now, for large values of N, the lowest value of λ in the ground-state solution dominates the partition function. In what follows, we will only consider the ground-state solution, so we drop the index k for simplicity.

(I) In the presence of an interface (trap) and an external constant magnetic field H_0 and in the absence of excluded volume effects, the external potential $U_{\mathrm{ext}}(x)$ can be written as

$$U_{\mathrm{ext}}(x) = -k_{\mathrm{B}}T\kappa\delta(x) - k_{\mathrm{B}}T\,\frac{(\chi_{\parallel} + \chi_{\perp})H_0^2 a}{4},\tag{3}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the longitudinal and perpendicular magnetic susceptibility components of the polymer chain, respectively. The interface is characterized by a positive value of the parameter κ in the case of the attraction of monomers by the interface and by a negative value of κ in the opposite case where the monomers push off from the interface. Note that κ has the dimension of a length which might be considered as the (microscopic) extension of a trap.

Then, the Edwards equation (1), which formally corresponds to the time-independent Schrödinger equation for the function u, takes the form

$$\lambda u(x) = -\frac{a^2}{6}\frac{d^2 u(x)}{dx^2} - \kappa\delta(x)u(x) - \frac{(\chi_{\parallel} + \chi_{\perp})H_0^2 a}{4}u(x),\tag{4}$$

where the x axis is directed perpendicularly to the interface. In such a linear system, a localized polymer state can exist only in the case of an attractive interface ($\kappa > 0$).

The solution of Eq. (4) reduces to solving the homogeneous equation

$$\frac{a^2}{6}\frac{d^2 u(x)}{dx^2} + \lambda u(x) + \frac{(\chi_{\parallel} + \chi_{\perp})H_0^2 a}{4}\,u(x) = 0\tag{5}$$

in the regions $x > 0$ and $x < 0$ with the following boundary conditions at $x = 0$:

$$u\,|_{+0} = u\,|_{-0},\tag{6}$$

$$\frac{du}{dx}\bigg|_{+0} - \frac{du}{dx}\bigg|_{-0} = -\frac{6}{a^2}\kappa u\bigg|_{0}.\tag{7}$$

The localized (ground) state solution of Eq. (5) satisfying the boundary conditions (6) and (7) reads

$$u(x) = \frac{\sqrt{3\kappa}}{a}e^{-3\kappa|x|/a^2},\tag{8}$$

and the eigenvalue λ corresponding to this localized state is equal to

$$\lambda_l = -\frac{3\kappa^2}{2a^2} - \frac{(\chi_{\parallel} + \chi_{\perp})H_0^2 a}{4}.\tag{9}$$

The region of localization of the solution is characterized by the localization length $L \sim a^2/(3\kappa)$.

If we describe the real chain in a self-consistent field, we suppose the interactions between monomers are repulsive and local. The presence of other segments provides a repulsive potential proportional to the density $c(x)$ [7, 11, 12]: $U_{\mathrm{ev}}(x) = k_{\mathrm{B}}Tvac(x)$, where v is the (dimensionless) excluded volume parameter. Consequently, one can describe each chain as an ideal chain subjected to an external potential $U_{\mathrm{ev}}(x)$. The density $c(x)$ is proportional to $c(x) \sim |u(x)|^2$ for the ground state dominance (GSD) [7]. Thus, Eq. (1) can be rewritten as follows:

$$\lambda u = -\frac{a^2}{6}\frac{d^2 u}{dx^2} + va|u|^2 u + \frac{1}{k_{\mathrm{B}}T}U_{\mathrm{ext}}(x)u.\tag{10}$$

In the presence of an interface, in an external constant magnetic field, the external potential $U_{\mathrm{ext}}(x)$ takes the form (3), and the nonlinear equation for a real polymer chain takes the following final form:

$$\lambda u = -\frac{a^2}{6}\frac{d^2 u}{dx^2} + va|u|^2 u - \kappa\delta(x)u-$$

$$-\frac{(\chi_\parallel + \chi_\perp)H_0^2 a}{4}u. \tag{11}$$

Let us rescale the variables according to

$$\frac{2}{|v|}\left\{\lambda + \frac{(\chi_\parallel + \chi_\perp)H_0^2 a}{4}\right\} \rightarrow \lambda,$$

$$\frac{2\sqrt{3}}{a\sqrt{|v|}}\kappa \rightarrow \kappa, \qquad \frac{x}{l} \rightarrow x, \tag{12}$$

where $l = a/\sqrt{3|v|}$ is the excluded volume length (EV-length). By introducing the dimensionless state function according to $\sqrt{a}u \rightarrow u$, we can rewrite SNLSE (11) in the following standard form:

$$\lambda u = -\frac{d^2u}{dx^2} + 2\sigma|u|^2 u - \kappa\delta(x)u, \tag{13}$$

where the sign function $\sigma = \pm 1$ (excluded volume $v > 0$ and $v < 0$, respectively) stands for the repulsion and the attraction between monomers, respectively.

In order to return to the initial parameters of the system, transformations (12) have to be applied once.

The solution of Eq. (13) is reduced to solving the corresponding homogeneous equation in the regions $x > 0$ and $x < 0$ supplemented with the following boundary conditions at $x = 0$ (see [13]):

$$u\mid_{+0} = u\mid_{-0}, \tag{14}$$

$$\left.\frac{du}{dx}\right|_{+0} - \left.\frac{du}{dx}\right|_{-0} = -\kappa u\big|_0. \tag{15}$$

As the ground state is dominant, we can omit the modulus and rewrite Eq. (13) in the regions outside the interface in the form

$$\frac{d^2u}{dx^2} + \lambda u - 2\sigma u^3 = 0. \tag{16}$$

Our physical system corresponds to the case of the repulsion between monomers $\sigma = +1$ (excluded volume $v > 0$) and the attraction of monomers by the interface ($\kappa > 0$). In this case, we have the following expression for the solution satisfying the boundary conditions and having zero density far from the interface ($u(x) \rightarrow 0$ as $|x| \rightarrow \infty$):

$$u(x) = \frac{\xi}{\sinh[\xi(|x| - x_0)]}, \tag{17}$$

where the parameter ξ is equal to

$$\xi = \sqrt{-\lambda}. \tag{18}$$

The parameter x_0 can only be negative. The value of the parameter λ is always negative regardless of the magnitude of the field H_0.

Solution (17) is completely characterized by the value of the parameter ξ (or λ). The parameter x_0 is expressed in terms of ξ due to the boundary condition (15) which can be rewritten for our solution (17) as

$$2\xi\coth(\xi x_0) = -\kappa. \tag{19}$$

It can be seen from this relation that, as a consequence of $x_0 < 0$, κ can only be positive in the case of $v > 0$, i.e., the localized state exists only in the case of attracting interface.

Equation (13) requires the condition of normalization which defines, in fact, the total number of monomers per (dimensionless) unit area:

$$N = \int_{-\infty}^{+\infty} |u(x)|^2 dx. \tag{20}$$

We note that, in the standard framework of the mean-field approach, all monomers in the system are considered to belong to a single chain, and particular effects of the chain ends are ignored. For simplicity, we denote N as the total number of monomers in the system.

Note that, in contrast to the case of a linear system (see Eq.(4)), the normalization in the nonlinear case leads to a relation between the parameters ξ and N (or λ and N). Substituting our solution (17) in integral (20) and taking relation (19) between x_0 and ξ into account, we can finally obtain the dependence $N = N(\xi)$ or, *vice versa*, $\xi = \xi(N)$ (or $\lambda = \lambda(N)$). For our system ($v > 0; \kappa > 0$), we arrive at the following result:

$$N = \kappa - 2\xi. \tag{21}$$

It is shown in [13] that three different types of nonlinear localized states can exist for Eq. (13) depending on the relations between the parameters v and κ. In the first case ($v < 0; \kappa > 0$), the interface is attractive, and the maximum of the amplitude of a localized state is at the point of the interface (trap). The localized state in the case ($v < 0; \kappa < 0$) has the amplitude maxima located symmetrically on both sides of the interface. The last (third) case ($v > 0; \kappa > 0$) corresponds to our physical situation.

The maximum value of parameter N in our case is equal to $N_{\text{sat}} = \kappa$. This point corresponds to the limit case of $\lambda \to 0$ (or $\xi \to 0$). No more monomers can be added to the interface in this case. Thus, this point corresponds to the *saturated state* of the interface. We note that the eigenvalue of the linear system λ_l is given in rescaled units by

$$\lambda_l = -\kappa^2/4. \tag{22}$$

Equation (13) can be alternatively derived from a variational principle using the energy functional $E[u]$ (see [7]):

$$E = \int\limits_{-\infty}^{+\infty} \left[\left| \frac{\partial u}{\partial x} \right|^2 + \sigma |u|^4 - \kappa \delta(x) |u|^2 \right] dx. \tag{23}$$

Substituting our solution (17) in Eq. (23) and using expression (21), we find the following relation between the total energy E and the total number of monomers in the chain N (see [13]):

$$E = \lambda_l N - \frac{N^3}{12} + \frac{\kappa N^2}{4}. \tag{24}$$

The first term in this relation describes the energy of N non-interacting monomers in the chain and corresponds to the description of the system in the linear approximation; the second term describes the energy of interaction of monomers in a pure solution (as if the interface were absent); and the third term describes the interaction of bound monomers through an interface. Note that the sign of the trap (sign of κ) determines only the last term. For $\kappa > 0$, the presence of an attractive interface *increases* the energy of the localized state (the interface attracts the monomers which repel each other).

Differentiating expression (24) with respect to N and using relation (21) for $N(\xi)$, we can easily verify the validity of the relation $\partial E / \partial N = \lambda$. So, the eigenvalue λ plays the role of *chemical potential* for monomers bound in the localized state.

(II) Let us describe a polymer chain in the system of *two penetrable interfaces*. In the presence of two interfaces, the external potential $U_{\text{ext}}(x)$ in the initial variables has the following form (compare with (3)):

$$U_{\text{ext}}(x) = -k_{\text{B}} T \kappa [\delta(x+d) + \delta(x-d)] -$$

$$- k_{\text{B}} T \frac{(\chi_{\parallel} + \chi_{\perp}) H_0^2 a}{4}, \tag{25}$$

where the interfaces are characterized by the value of the parameter κ. As before, in the case of attraction

of monomers by the interfaces, the parameter κ is positive, $\kappa > 0$, the x-axis is directed perpendicularly to the interfaces, and $2d$ is the distance between the interfaces.

Using transformations (12), by means of which Eq. (13) had been obtained, we obtain the rescaled SNLSE as follows:

$$\lambda u = -\frac{d^2 u}{dx^2} + 2\sigma |u|^2 u - \kappa [\delta(x+d) + \delta(x-d)] u. \tag{26}$$

Here, the sign function $\sigma = \pm 1$ for repulsion and attraction between monomers, respectively, and, as before, we use the initial symbols of the variables λ, x, d and κ.

Equation (26) is reduced to the corresponding homogeneous equation of the form (16) in the regions outside the interfaces with the following boundary conditions:

$$u \mid_{\pm d + 0} = u \mid_{\pm d - 0}, \tag{27}$$

$$\left. \frac{du}{dx} \right|_{\pm d + 0} - \left. \frac{du}{dx} \right|_{\pm d - 0} = -\kappa u \mid_{\pm d}. \tag{28}$$

Again, we consider a positive excluded volume ($\sigma = +1$) and the attraction of monomers by the interfaces ($\kappa > 0$). For a positive excluded volume, three different types of stationary localized states can exist [14]: in-phase symmetric state (IS), antisymmetric state (A), and antiphase asymmetric (inhomogeneous) state (AA). The state with the asymmetric distribution of the density near two interfaces splits off in a bifurcation way from the antisymmetric solution. However, as the ground state is dominant, we are only interested in the *in-phase symmetric solution* (IS) which has the following form in the regions $x < -d$ (1), $x > d$ (2) and $|x| < d$ (3):

$$u_{1,2}(x) = \mp \frac{\xi}{\sinh[\xi(x - x_{1,2})]}, \quad u_3(x) = \frac{q'\eta}{\text{cn}(\eta x, q)}, \tag{29}$$

where $x_2 < d$ and $x_1 = -x_2$. Here, $\text{cn}(\eta x, q)$ is the Jacobi elliptic function with modulus q. Also, we introduce

$$q' = \sqrt{1 - q^2} \quad \text{and} \quad \eta = \xi / \sqrt{2q^2 - 1}, \tag{30}$$

where ξ is defined in (18). The elliptic modulus q varies in the range from $1/\sqrt{2}$ to 1.

The advantage of our method to compare with other approaches is that we deal with the exact solution. This makes it possible to consider all piecewise constant potential forms in a straight forward manner. Solution (29) is one-parameter and is completely characterized by the value of the parameter ξ (or λ). Other two parameters

q and x_1 (or x_2) are expressed in terms of ξ from the boundary conditions (27) and (28) which can be rewritten for our solution (29) as

$$\frac{\xi}{\sinh[\xi(d - x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)}, \qquad (31)$$

$$\frac{q'\eta^2 \text{sn}(\eta d, q)\text{dn}(\eta d, q)}{\text{cn}^2(\eta d, q)} + \frac{\xi^2 \cosh[\xi(d - x_2)]}{\sinh^2[\xi(d - x_2)]} =$$

$$= \frac{\kappa\xi}{\sinh[\xi(d - x_2)]}. \qquad (32)$$

Because two interfaces attract the monomers, a convenient characteristics of a localized state is represented by the *amplitudes* $A_1 = u(x = -d)$ and $A_2 = u(x = d)$ at these interfaces [3, 14, 15]. Via the symmetry of the localized state, we can denote $A_1 = A_2 \equiv A$. Then the boundary conditions (31) and (32) can be rewritten in terms of the amplitude A as follows:

$$A = u(-d) = u(d) = \frac{\xi}{\sinh[\xi(d - x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)}, \quad (33)$$

$$\sqrt{A^2 - q'^2\eta^2}\sqrt{A^2 + q^2\eta^2} + A\sqrt{A^2 + \xi^2} = \kappa A. \qquad (34)$$

Equation (34) can be reduced to the form

$$\sqrt{A^4 + A^2\xi^2 - q^2 q'^2 \eta^4} + A\sqrt{A^2 + \xi^2} = \kappa A. \qquad (35)$$

These three relations (33), (34) (or (33), and (35)) determine the parameters A, x_2, and q as functions of the parameters ξ and d. In the general case, it can be exactly resolved numerically.

However, a solution can be obtained analytically for the limiting cases $\kappa d \gg 1$ and $\xi \to 0$ (or $\lambda \to 0$). In the limit $\kappa d \gg 1$ (week coupling between interfaces), the problem is reduced to the study of the effective system of two coupled anharmonic oscillators with a "hard" nonlinearity, when the eigenvalue λ increases with the amplitude of the solution. This problem is described analytically in more details in [14].

After the substitution of our (IS) solution (29) into integral (20) defining the total number of monomers in the chain, we can finally obtain the dependence $N = N(\xi)$ and the inverse dependence $\xi = \xi(N)$ (or $\lambda = \lambda(N)$) which is presented in Fig. 1. It can be shown that the dependence for (IS) state terminates at the edge of the spectrum of linear waves ($\lambda = 0$), and the profile of this spatially localized state near the interfaces has
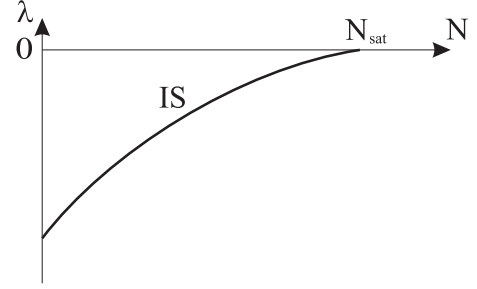

Fig. 1. Dependence $\lambda(N)$ for the in-phase symmetric (IS) state in the system with a positive excluded volume

the form of algebraic solitons with power-law asymptotic behavior at large distances [16]. This case corresponds to the situation where the total number of monomers tends to its maximum value. A total number of monomers greater than the maximum value N_{sat}, corresponding to the boundary of the band of linear bulk waves $\lambda = 0$, can not be localized in the system.

Taking the symmetry of the in-phase symmetric (IS) solution (29) into account and calculating the total number of monomers, we come to the following exact result:

$$N = \int_{-\infty}^{+\infty} |u|^2 dx = 2\xi[\coth[\xi(d - x_2)] - 1] + 2\eta \times$$

$$\times \frac{\text{sn}(\eta d, q)\text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - 2\eta \text{E}(\text{am}(\eta d, q), q) + 2q'^2\eta^2 d, \quad (36)$$

where $\text{E}(\varphi, q)$ is the elliptic integral of the second type, and $\text{am}(\varphi, q) = \arcsin[\text{sn}(\varphi, q)]$ is the elliptic amplitude. Two parameters $x_2 = x_2(\xi, d)$ and $q = q(\xi, d)$ are determined from the boundary conditions (33),(34) (or (35)).

Using relation (31), we can eliminate the parameter x_2 and then rewrite Eq. (36) in the form

$$N = 2\left[\sqrt{\frac{q'^2\eta^2}{\text{cn}^2(\eta d, q)} + \xi^2} - \xi\right] + 2\eta\frac{\text{sn}(\eta d, q)\text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} -$$

$$-2\eta \text{E}(\text{am}(\eta d, q), q) + 2q'^2\eta^2 d. \qquad (37)$$

Let us study the behavior of the system at the *saturation point* defined by

$$\lambda \to 0 \quad \text{and} \quad \xi \to 0. \qquad (38)$$

In this case, we can rewrite solution (29) for $u_{1,2}(x)$ in the form

$$u_{1,2}(x) = \mp\frac{\xi}{\sinh[\xi(x - x_{1,2})]} \approx \mp\frac{1}{x - x_{1,2}}, \qquad (39)$$
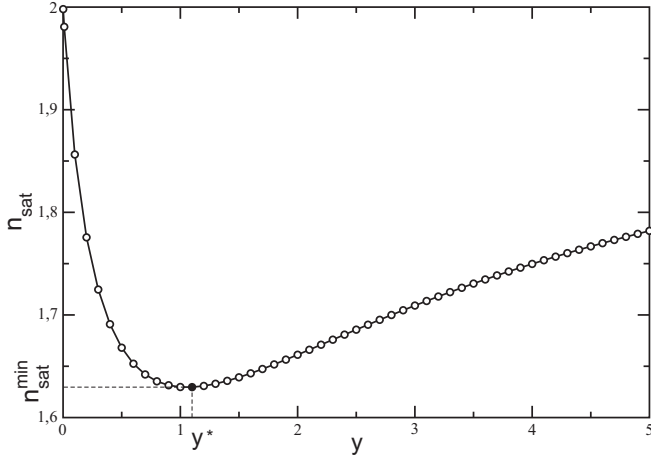
Fig. 2. Dependence $n_{\mathrm{sat}}(y)$ at the saturation threshold

and, as it follows from (33), the amplitude at the interface is equal to

$$A \approx \frac{1}{d - x_2}. \tag{40}$$

If we suppose that $\eta d \ll 1$, then (33) yields $A \approx q'\eta \ll 1$. Substituting this expression into the boundary condition (34) (or (35)), we come to the following result for the parameter q:

$$q^2 \approx \frac{1}{2}(1 + \frac{\xi^2}{2\kappa^2}). \tag{41}$$

However, this means that the parameter η, which is equal to

$$\eta = \frac{\xi}{\sqrt{2q^2 - 1}} \approx \sqrt{2}\kappa , \tag{42}$$

is not small in the limiting case $\eta d \ll 1$ because the parameter κ has an arbitrary value. This means that the parameter q is close to $1/\sqrt{2}$. Thus, the inequality $\xi \ll 1$ leads to the limit case for the parameter q, viz., $q \to 1/\sqrt{2}$.

We now suppose that the distance d is not small. The amplitude A is not small too, and the boundary condition (33) can be rewritten as

$$A \approx \frac{1}{d - x_2} \approx \frac{1}{\sqrt{2}} \frac{\eta}{\mathrm{cn}(\eta d, 1/\sqrt{2})}. \tag{43}$$

In this case, the dependence of the parameter $q = q(\xi, d)$ (or, equivalently, $\eta = \eta(\xi, d)$), which is necessary in order to obtain N in (37), should be found after the substitution of A from (43) in the boundary condition

(35). In this general case, as a result of this substitution, we come to the following equation for the variable η:

$$\eta^2 \mathrm{cn}^3(\eta d, 1/\sqrt{2}) + 2\kappa^2 \mathrm{cn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2}\kappa\eta = 0. \tag{44}$$

It is now possible to reduce one variable by introducing the *scaling variables*

$$g_\eta = \eta/\kappa \quad \text{and} \quad y = \kappa d. \tag{45}$$

We note the y gives the *overlap* of the interfaces profiles in terms of the linear solution. Here, $y \ll 1$ corresponds to strongly overlapping interfaces, and $y \gg 1$ corresponds to a week overlap. Using Eq. (45), we obtain

$$g_\eta^2 \mathrm{cn}^3(g_\eta y, 1/\sqrt{2}) + 2\mathrm{cn}(g_\eta y, 1/\sqrt{2}) - 2\sqrt{2}g_\eta = 0 \tag{46}$$

with the formal solution $g_\eta(y)$. Further, we will use this function for the calculation of the physical characteristics of the system, such as the number of monomers trapped between interfaces/surfaces, energy of the system, and force acting between two penetrable traps.

We now introduce the reduced monomers number $n_{\mathrm{sat}} = N_{\mathrm{sat}}/\kappa$. Then, in the saturation limit $\xi \to 0$ ($N(\xi, d) \to N_{\mathrm{sat}}(d)$), we have $q \to 1/\sqrt{2}$, and expression (37) transforms into

$$n_{\mathrm{sat}} \approx \frac{\sqrt{2}\, g_\eta}{\mathrm{cn}(g_\eta y, 1/\sqrt{2})} + 2g_\eta \frac{\mathrm{sn}(g_\eta y, \frac{1}{\sqrt{2}})\mathrm{dn}(g_\eta y, \frac{1}{\sqrt{2}})}{\mathrm{cn}(g_\eta y, \frac{1}{\sqrt{2}})} -$$

$$-2g_\eta \mathrm{E}(\mathrm{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}) + g_\eta^2 y. \tag{47}$$

Here, the function $g_\eta(y)$ is the solution of Eq. (46). Thus, the solution of Eq. (47) has the universal (scaling) form: $n_{\mathrm{sat}} = n_{\mathrm{sat}}(y)$ for different values of the parameters κ and d. The numerical solution for $n_{\mathrm{sat}}(y)$ is presented in Fig. 2. Starting from a large distance d between interfaces (week overlap, $y \gg 1$), the saturation parameter n_{sat} decreases with d as the "bridge" (formed by the overlapping tails of the profile) between interfaces becomes more powerful and tends to its minimum value $n_{\mathrm{sat}}^{\min} \approx 1.63$ at a characteristic distance given by the value $y^* \approx 1.11$. It increases again for $d \to 0$, when monomers start to escape outside the region confined by two penetrable interfaces into the tails on the both sides of the interfaces, and reaches its maximum value $n_{\mathrm{sat}}^{\max} = 2$ for $d = 0$ (strong overlap, $y \ll 1$).

In the limiting case $y \ll 1$ (strong overlap), we have $g_\eta \approx \sqrt{2} - 2\sqrt{2}y$ and obtain the following result for the function n_{sat} from Eq. (47):

$$n_{\mathrm{sat}} \approx 2 - 2y. \tag{48}$$
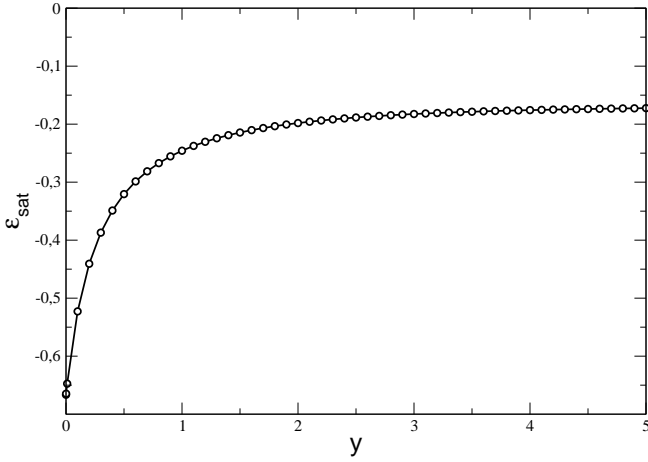
Fig. 3. Dependence $\varepsilon_{\mathrm{sat}}(y)$ at the saturation threshold

Fig. 4. Dependence $\varepsilon_{\mathrm{sat}}(n_{\mathrm{sat}})$ at the saturation limit

Here, we took the correction to expression (41) for the parameter q into account: $q^2 \approx \frac{1}{2}(1 + \frac{\xi^2}{2\kappa^2}) + 2y$.

In the opposite limiting case $y \gg 1$, the interaction (overlapping) between two traps is small only in the small-amplitude limit, where the description of the system can be reduced to a model of coupled "hard" anharmonic oscillators [14]. Such a description is valid only in the region $1 - \lambda/\lambda_l \ll |\lambda_l|$, where the eigenvalue $\lambda_l = -\kappa^2/4$ ($\xi = \kappa/2$).
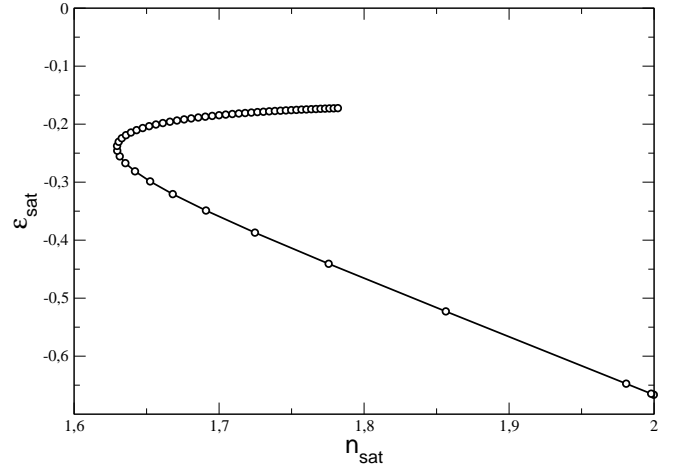
The distance d between two interfaces can not be of an arbitrary length. It is limited by the maximum length of a chain, $viz.$, by the total number of monomers multiplied by the statistical segment length of the chain, $d_{max} = (N-1)a$. The minimal distance d_{min} is defined by the parameter a.

The total energy (per unit area) of the system, E, is defined by the integral

$$E = \int\limits_{-\infty}^{+\infty} \left\{ \left|\frac{\partial u}{\partial x}\right|^2 + \sigma|u|^4 - \kappa[\delta(x+d) + \delta(x-d)]|u|^2 \right\} dx.$$

(49)

Substituting the ground-state solution (29) in Eq. (49) and taking the boundary condition (33) into account, we find the exact expression for the total energy of the system. Again, we can introduce the scaling variables y and g_η and define the appropriately reduced energy of the system $\varepsilon_{\mathrm{sat}} = E_{\mathrm{sat}}/\kappa^3$. Then, in the limit case $\xi \to 0$, we obtain

$$\varepsilon_{\mathrm{sat}} \approx \frac{\sqrt{2}\, g_\eta^3}{3\mathrm{cn}^3(g_\eta y, 1/\sqrt{2})}[1 + \sqrt{2}\mathrm{sn}(g_\eta y, 1/\sqrt{2}) \times$$

$$\times \mathrm{dn}(g_\eta y, 1/\sqrt{2})] - \frac{g_\eta^2}{\mathrm{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}.$$

(50)

Using the solution $g_\eta(y)$ given by Eq. (46), we obtain the function $\varepsilon_{\mathrm{sat}}(y)$ of a single variable. The minimum value of $\varepsilon_{\mathrm{sat}}$, as it follows from (50), is equal to $\varepsilon_{\mathrm{sat}}^{\min} = -2/3$. The universal dependence $\varepsilon_{\mathrm{sat}} = \varepsilon_{\mathrm{sat}}(y)$ is presented in Fig. 3. The energy of the saturated system is, thus, a monotonously increasing function of the distance between the traps. Note that the condition of saturation, however, implies the exchange of chains by changing the distance according to the result given in Fig. 2. Thus, the system is considered in equilibrium with free chains in a highly dilute solution ($c \to 0$) which populate the interfaces until the saturation is reached. Note that there is no contradiction between the requirement of saturation and a highly diluted bulk solution for an adsorption strength per monomer (related to κ) of the order of a few kT [17]. In particular, for changes of the distance between the interfaces, where the saturation value n_{sat} is decreased, chains have to be released because of the over-saturation (positive free energy excess).

In Fig. 4, we display the dependence of the function $\varepsilon_{\mathrm{sat}}(n_{\mathrm{sat}})$. It clearly indicates two different values (branches) of the total excess energy of the two-interface system for the same value of the total number of monomers N localized at the interfaces. These branches corresponding to the same value of the parameter N are related to two different distances between interfaces d_1 and d_2, which can be easily seen from the dependence for the total number of monomers presented in Fig. 2. Thus, there exist a high-energy phase (large separation) and a low-energy phase (close interfaces).

Thus, we have described the localized states with zero bulk concentration ($u(x) \to 0$ for $|x| \to \infty$) having "dynamical" equilibrium at the saturation limit. This can be realized for highly diluted bulk solutions and strongly attracting interfaces, as discussed above. We obtained exact solutions for the problem of adsorption of real polymer chains in systems containing two adsorbing interfaces placed in an external constant magnetic field within the mean-field approximation. Using the exact solution for the SNLSE on intervals of constant potentials opens the possibility to treat various localization problems for polymer chains in such environments using the appropriate boundary conditions.

For the case of zero bulk concentration, we have considered the polymer layer at the saturation limit. This scenario is realized if the adsorption takes place from a highly diluted polymer solution. Because of the huge gain of free energy per chain in the polymer adsorption, the highly diluted polymer solutions lead to saturated surface states (see [7]). For the saturation limit, we have derived an exact scaling solution, where the only relevant control parameter is the measure of the overlap between the interfaces given by the scaling variable which can be considered as the coupling parameter of the interface-polymer system. We have found that the saturation density of monomers behaves non-monotonically as a function of the distance between the interfaces. When the distance becomes small, the polymer double layer can relax excluded volume constraints by forming larger loops and tails in the outside region of the interfaces. The changing of the distance between the interfaces changes the number of chains adsorbed. We have found also the exact expression for the energy of the system which turned out to be strictly negative. The non-monotonous behavior of the saturation density of polymers as a function of the distance between the interfaces results in the "two-phase" behavior of the free energy as a function of the amount of adsorbed polymers (see Fig. 4). The low-energy phase corresponds to small distances between the interfaces, and the high-energy phase corresponds to large distances between them.

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ЛОКАЛІЗАЦІЯ ПОЛІМЕРНОГО ЛАНЦЮЖКА
ПОБЛИЗУ ДВОХ ПРОНИКНИХ ПОВЕРХОНЬ
ПОДІЛУ В ПОСТІЙНОМУ МАГНІТНОМУ ПОЛІ

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Р е з ю м е

Досліджено локалізацію полімерного ланцюжка в системі двох проникних інтерфейсів у зовнішньому постійному магнітному полі в наближенні середнього поля. Вивчено стан насичення полімерного ланцюжка в граничному випадку нульової концентрації в об'ємі на великій відстані від інтерфейсів. Одержано немонотонну поведінку залежності кількості адсорбованих полімерів від відстані між інтерфейсами.